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The generation of Ni emitter for field ionization

N F Zahran
Department of Physics, Atomic Energy Authority, Cairo, Egypt

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Conditioned tungsten wires find much use in field ionization mass spectrometry because they offer large emission currents (Beckey *et al* 1969 and Matsuo *et al* 1979). Weightman *et al* (1975), Bursey *et al* (1976) and Rechsteiner *et al* (1977), prepared field emitters by cathodic metal deposition on tungsten wires from aqueous solutions of simple salts by using a pulse generator connected with a dc power supply.

Goldenfeld and Veith (1981) used a drop cell method in conjunction with a dc supply to prepare dendritic emitters. Recently, Zahran *et al* (1987) used, for the first time, normal sine waves in the drop cell method.

The aim of the present paper is to carry out a study using the developed drop cell technique (Zahran *et al* 1987) to prepare a dendritic emitter surface of Ni.

A 10 μm tungsten wire is spot-welded onto the emitter supports. The supports are fixed in a movable vertical column. The electrodeposition of Ni dendrites is performed in the following way. A drop of 0·5 M $Ni(NO_3)_2$ solution is placed between two fixed platinum ribbons 0.5 mm in thickness and 1 mm apart by using a syringe. Then, by the aid of a microscope, the 10 μm wire is adjusted inside the drop to the required position. The electric circuit used for the electrodeposition of Ni dedrites is shown in Figure 1. A time gate is connected to the sine wave supply, and a selected number of sine waves can be controlled. The current strength through the electrolytic cell is measured by an oscilloscope connected across a sampling resistor.

Trials were attempted for electro-deposition of metallic Ni from $Ni(NO_3)_2$ aqueous solution drop on tungsten wire using either dc or ac power sources. The deposits obtained were examined by a scanning electron microscope and the corresponding electron micrographs (Figures 2 and 3, respectively) showed two morphological structures. As can be seen in Figure 2, the use of 5 dc pulses at 3 V and pulse duration 5×10^{-2} sec. leads to the production of coarse-grained Ni deposit. On the other hand, by using an ac source of the normal 50 Hz sine wave at 3 V for 3 minutes a finer grained Ni deposite is produced as shown in Figure 3.

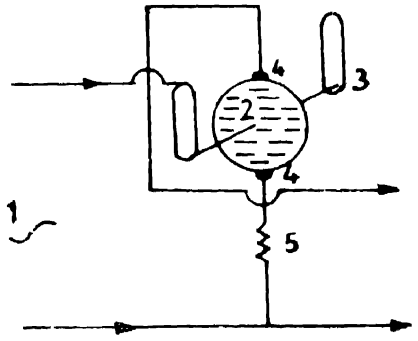

Figure 1. Electric used for the electrodeposition of Ni on tungsten.
1. 50 Hz sine wave
2. drop of Ni (NO_3) solution
3. 10 μm tungsten wire
4. Platinum electrodes
5. Sampling resistor connected to an oscilloscope

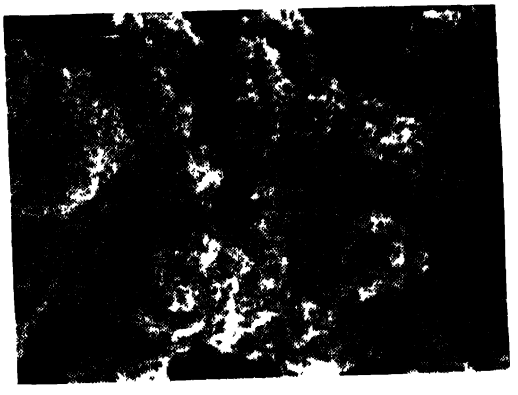

Figure 2. Electron micrograph of Ni layer on tungsten wire after 5 pulses at 3V dc (1000x).

Figure 3. Electron micrograph of Ni dendrites on tungsten after 3 min. at 3V ac (1000x).

The ac pulse shape, as observed through a sampling resistor connected to an ocilloscope during electrodeposition, is changed from a sine wave to a partially rectified one (Figure 4). The theoretical foundation of ac electrolysis was first considered by Warburg (1899). Doss and Agrawal (1950 and 1951) reported that when an alternating field was connected to two platinum electrodes dipped in an aqueous electrolytic system, a dc potential could be detected at each electrode.

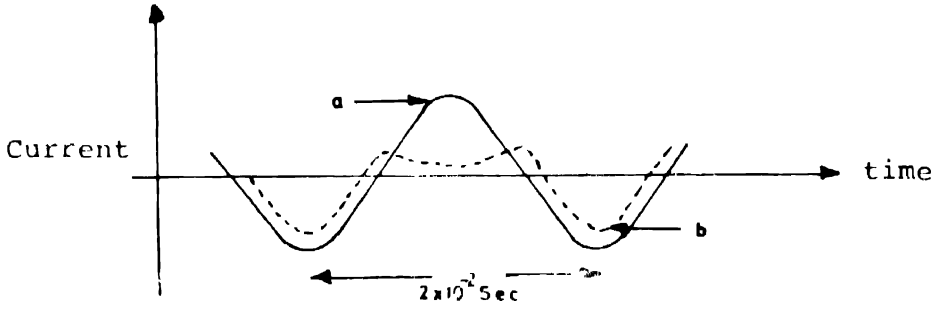

Figure 4. Changes in the ac pulse shape during electrodeposition.
a. The applied pulse
b. The rectified pulse

Later, this experimental fact was well defined as a Faraday rectification phenomenon by Oldham (1957) and Fleischman and Oldham (1958).

Observations of the process of elecrolytic ac deposition of Ni by the microscope show an evolution of gas bubbles.

It is also observed, that the time of deposition of the coarser grained deposit (2.5×10^{-1} sec.) is very short in comparison with the needed for the formation of the finer grained deposit during the cathodic half wave of ac (1.5 min.). This is in agreement with Wranglen's (1960) observation that redissolution of the cathode deposits often occurred during deposition with periodically reversed current in the solution. The redissolution phenomenon means a reversed current i.e., the net result is a low current density.

Similarly, in the drop cell electrolyte, dissolution can occur during the anodic half wave. Therefore, different crystalline pits could be formed and irregular rolling-off layers occured, forming a rough surface. During the following cathodic half wave the surface is partially heated so that its roughness becomes permanent. During the next anodic half wave some crystals are partially dissolved and at the beginning of the cathodic half wave, numerous new crystals could be formed. The rate of crystal growth during the cathodic half waves is faster than that of dissolution during the anodic half waves, as can be concluded from the pulse shape. This is in accord with the faradic rectification phenomenon.

Field ionization mass spectrum of *n*-heptane taken with Ni emitter is shown in Figure 5. It is known that the intensity ratio of the fragment ion $C_2H_5^+$ to the molecular ion $C_7H_{16}^+$ in the field ionization mass spectrum of *n*-heptane characterises the field strength (Speier *et al* 1972). With the present emitter the

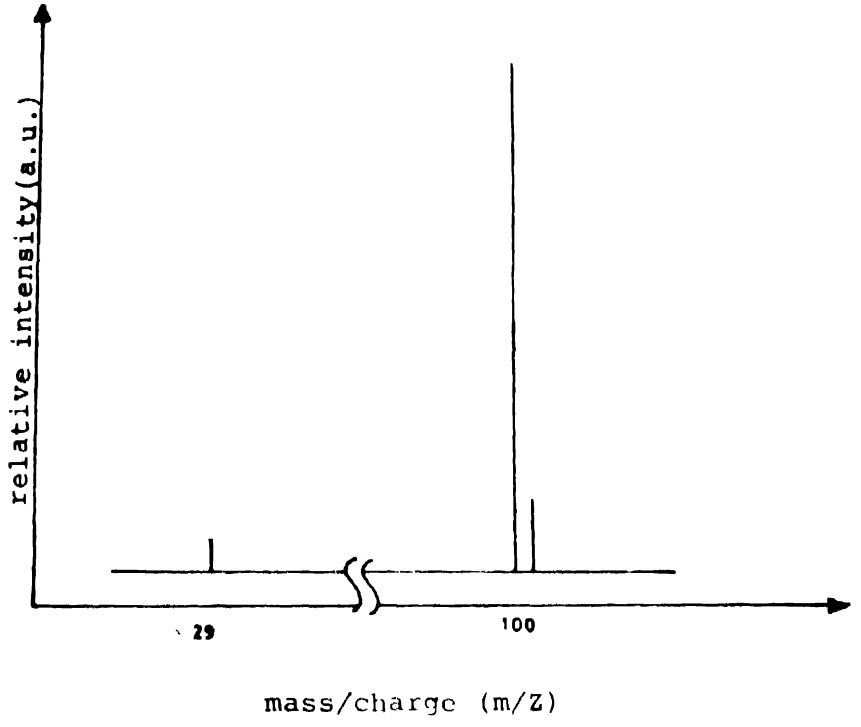

Figure 5. The field ionization mass spectrum of *n*-heptane using Ni on tungsten.

intensity ratio is about $1{\cdot}5 \times 10^{-2}$ which means, according to Speier et *al* (1972), a field strength of about 1.5×10^7 V/cm.

After production of the Ni emitter, a very weak ion emission is observed at room temperature. A high emission is achieved only after thermal treatment of the emitter up to about 500°C. This may mean that Ni-emitter is initially, formed in the oxide form which has a nonconducting or a semiconducting property. The increase of the ion emission after the thermal treatment is probably due to some changes from the oxide form to the metallic form i.e. an increase in the conductivity of the emitter layer.

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